

THE RECOVERY OF MAGNESIUM CHLORIDE

from

NATURALLY OCCURRING BRINES AND EVAPORITES

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SUMMARY AND CONCLUSIONS

As the potash industry shifts to Canadian evaporites which may contain carnallite and to natural brines of marine origin containing magnesium chloride, there may be a significant shift away from United States dependence on the sea water magnesia process to manufacture cell feed for electrolytic production of magnesium metal. This shift may be accelerated by or instrumental in initiating a new potash industry based on solution mining and solar evaporation of the brines from underground leaching of the carnallite deposits of the Western United States. Though little is known in practice about the compositions obtainable at the well head, the theoretical equilibrium brines from the solution mining of carnallite have potash concentrations that compare favorably with the natural brines from which potash is now recovered. At the same time these brines are rich in magnesium chloride. As a consequence, potash operations on either natural brines of marine origin or on synthetic brines from solution mining of carnallite provide a potentially low cost and virtually inexhaustible source of magnesium chloride for production of cell feed. To be economic, however, the brine on evaporation should not intercept the leonite face on the Janecke type diagram at ambient temperatures, since the co-product potash would in that case be lost in a form that would make its recovery difficult.

INTRODUCTION

Magnesium, in the combined forms, is the sixth most abundant element and the third most abundant metal in the earth's crust, but it is so reactive that it is never found in nature in the elemental state. As part of the rock forming minerals like magnesite, dolomite, olivine, and serpentine, it is combined in virtually insoluble forms. As part of soluble minerals like kainite ($\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$), leonite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$), langbeinite ($\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$), and carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), it is found in evaporite deposits, generally of marine origin, deep within the earth's crust. Since these minerals are soluble, they are found only in deposits protected from the percolation and leaching action of ground waters by an insoluble and impermeable mantle. Usually this mantle is from several hundred to many thousands of feet thick. Finally, as a

solute in marine-like brines, magnesium is common in surface and subterranean waters throughout the world. The oceans, which contain 0.13 percent magnesium, illustrate the inexhaustible nature of the reserve.

The recovery of magnesium from the rock forming minerals, usually by thermal decomposition, and from dilute brines such as seawater by precipitation with lime, is a frequent industrial practice but discussion is outside the scope of this paper. The recovery of magnesium as magnesium chloride from evaporites or natural brines of concentration greater than sea water has been of little industrial significance for economic and technological reasons. This is illustrated by the present and projected United States capacity for metallic magnesium as shown in Table 1. Present capacity is preponderantly based on the sea water magnesia process with an also-ran second place to thermal reduction and present no capacity dependent on recovery from the stronger natural brines. Projected capacity, however, though still weighted in favor of the sea water magnesia process, is partly based on the recovery of magnesium chloride as a byproduct of potash operations.

Though it is undoubtedly premature to consider one projected plant as evidence of a significant industrial shift, recovery of magnesium chloride from the waste brines of potash operations is due to receive more attention in the future.

INFLUENCE OF COMPOSITION OF SYLVITE ORES ON UNITED STATES PRACTICE

While the United States has relied preponderantly on the sea water magnesia process as a source of magnesium chloride for cell feed, certain of the European practice is oriented more towards use of by-product magnesium chloride, obtained mostly from the potash industry. The difference in emphasis may be due in whole or part to differences in the composition of the ores mined for potash; to the locale of the ore reserves, which may lead to a difficult transportation problem in one case and not another; and to the relative production rates of non-chloride forms of potash which reject magnesium chloride to waste.

Until quite recently the United States obtained most of its potash requirements from the evaporites of the Carlsbad area in New Mexico. Though carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) mineralization is reported at about the 800 foot level in these deposits, the sylvinite workings at about the 900 foot level are low in carnallite. As a result the only significant source of magnesium chloride in

*TABLE 1

<u>Plants in Operation</u>	<u>Location</u>	<u>Capacity Tons/Yr.</u>	<u>Process Basis</u>
Dow Chemical	Freeport, Texas	36, 000	Sea water magnesia
Dow Chemical	Velasco, Texas	46, 000	Sea water magnesia
Alabama Metallurgical	Selam, Alabama	6, 000	Thermal reduction of dolomite
Nelco Metals	Canaan, Conn.	5, 000	Silico thermic reduction
Total in Operation		93, 000	
<u>Projected New Plants</u>			
Harvey Aluminum	Port Angeles, Wash.	20, 000	Sea water magnesia
Standard Magnesium	Portland-Vancouver area	11, 000	Solar evaporation
Total Projected		31, 000	
<u>Grand Total</u>		124, 000	

* Adapted from Chemical Week Nov. 30, 1963, page 31.

area is in the waste liquor from the potassium sulfate operations of the International Minerals and Chemical Corporation.

However, production of magnesium chloride from the high sulfate liquors which result from the double decomposition of langbeinite ($2\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4$) with sylvite (KCl) involves formidable technical and economic problems. To a degree these problems were resolved and token amounts of magnesium were made at Austin, Texas in 1946 from bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) prepared at Carlsbad. This plant was shut down at the end of the war. Several other magnesium plants were also shut down and the diminished market of peacetime supplied by producers with a better economic base. However, after a brief respite, International Minerals magnesium chloride operations were resumed and a flake product containing approximately 5 mols of water of crystallization was produced until 1961.

Though other factors may have been decisive it is suspected that the ore composition and location of the major potash reserves in this country have had much influence on U.S. choice of process for manufacture of magnesium plant cell feed.

INFLUENCES ON THE POTASH INDUSTRY

The emphasis in the potash industry is changing. Gradual depletion of high grade New Mexico reserves and increase in world demand for potash has encouraged new plant construction in the prairie provinces of Canada. Concurrently there is also a rising interest in natural brines which contain a high enough concentration of potash to excite development. In either case the processes proposed frequently call for rejecting magnesium chloride as a valueless waste at a high concentration. The use of waste magnesium chloride from Canada seems remote since both locale and climate are unfavorable. However, waste liquors from potash operations on natural brines or brines derived from solution mining of carnallite may become a significant source of magnesium chloride in the future.

Two plants which recover potash from natural brines containing magnesium chloride are in operation now: Standard Magnesium Co. (4), (5), near Wendover, Utah, and the Dead Sea Works Ltd. (6), (7), (8), in Israel. Two plants are in a stage of active development: the Arab Potash Co. using brine from the Dead Sea (13), and Minera Bayovar S.A. using brine from the Sechura Desert of Peru. Several others are being studied.

CLASSIFICATION OF BRINES

Though in the broadest sense, all brines probably should be considered as having originated from the sea, it is useful to classify brines as either marine or terrestrial. The ionic ratios of marine brines are similar to the ratios obtained from an equivalent evaporation of sea water. As a characteristic these brines are high in magnesium chloride and magnesium sulfate and low in calcium. They are formed by the evaporation of reclusive seas and by ground water and precipitation leaching of cyclic salts blown inland from the oceans. The evaporation of brines of this type by either solar or mechanical means can be expected to follow the normal progressions described by Van't Hoff (2), D'Ans (3), and others. Since most of the potash crystallizes as a double salt containing magnesium sulfate, recovery of potassium chloride from brines similar to the Great Salt Lake or to the bitterns from solar salt pans had not met with any commercial success to date.

The terrestrial brines are frequently high in calcium chloride and, as a result, low in sulfate. They are formed by groundwater percolation and leaching from the surrounding countryside or from subterranean evaporite deposits of perhaps secondary deposition. As a result, the composition of these brines is not restricted by the ionic ratios characteristic of evaporated sea water, and recovery of potassium chloride as sylvite or carnallite is possible. The brines of the Dead Sea or those from the geothermal wells near the Salton Sea are examples of this category.

As a third classification, brines of volcanic origin may contain carbonates and borates and also be high in sulfates. An example is Searles Lake in California.

The composition of natural brines may fall in between these categories as a result of formation from marine, terrestrial and/or volcanic sources. Excluding the volcanic deposits, recovery of values is dependent on the ratios of potassium, magnesium and sulfate. Synthetic brines obtained from solution mining of deposits of carnallitic evaporite normally would be classified as marine. Recovery of potassium chloride (KCl) may nevertheless be possible since mining can be to some extent selective. The relatively slow rate of solution of the sulfate salts may perhaps be utilized to advantage. Typical brine concentrations of marine and/or terrestrial origin are shown in Table 2.

TABLE 2
A COMPARISON OF SEA WATER WITH VARIOUS BRINE SOURCES

Typical Composition, mols/1000 mols water					
	Typical Sea Water(11)	Great Salt Lake Salt Pan Bitterns(5)	Dead Sea (Jordan)	Bonneville (Utah)(5)	Bocana de Virrila, Sechura (Peru)(12)
KCl	0.09	3.5	1.6	1.6	3.6
NaCl	4.3	39.7	14.3	42.4	40.9
CaCl ₂	0.2	0.2	8.2	0.6	0.2
MgCl ₂	0.5	7.1	29.6	2.5	31.9
MgSO ₄	0.5	11.3	0.2	0.9	13.5

APPLICATION OF SOLAR EVAPORATION IN THE RECOVERY OF MAGNESIUM CHLORIDE

Solar evaporation depends on conversion of the radiant energy of the sun to latent and sensible heat in the pan vapor. Geographical areas are suitable which have:

1. The highest solar gain, favoring areas closest to the equator.
2. Steady winds of low humidity to remove the pan vapors as they are formed.
3. Low annual rainfall, high evaporation rate relative to rainfall, or seasonal rainfall in the cool portion of the year.
4. An impermeable soil, preferably clay to minimize leakage. In some cases semi-pervious soils may be satisfactory if the brine table is high and losses are only by diffusion to the reservoir.
5. Level terrain of sufficient area to permit construction of new pans and abandonment of these pans as they fill with salt. In lieu of additional area, an adequate supply of flushing water to remove the salt periodically, allowing reuse of the pans.

On suitable potash brines, which deposit substantially all of the potash values as carnallite, immense amounts of magnesium chloride are rejected in the waste streams. In a plant proposed for operation at the Dead Sea at a rate of 250,000 tons of potash a year, more than 300,000 tons of magnesium chloride as bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) could be produced from the decomposition liquor, and over 3 million tons additional recovered from the pan bitterns.

Solution Mining and Solar Evaporation of Brines Derived From Carnallite

The carnallite evaporite deposits of the Western U.S. are located in arid regions where solar evaporation may be feasible. Provided all criteria are satisfied, and if solution mining can be successfully employed, reserves of both potash and magnesium chloride in this country may be significantly increased. Deposits in the vicinity of the Paradox Basin in Utah have been reported to be as much as 200 feet thick (9). In Grand county a section containing as much as 60 percent carnallite and 140 feet thick have been located in Canada. Some deposits such as the Prairie evaporites (10) of the Williston Basin in North Dakota, are found at depths of 8,000 feet and may be beyond the reach of solution mining techniques.

As a speculation it is interesting to assume a solution mining condition in which equilibrium is obtained in the well equivalent to saturation at 30 degrees C for the four component system NaCl-KCl- MgCl_2 - H_2O . In that case the brine at the well head contains:

<u>Component</u>	<u>Percent</u>
KCl	3.4
NaCl	1.4
MgCl_2	26.4
H_2O	68.8

Solar evaporation of this brine to the bischofite boundary removes 34 percent of the initial water and recovers 90% of the potash as carnallite in one cycle. The weight ratio of potassium chloride to sodium chloride in the residual solids after decomposition of the carnallite is 2.0, whereas the ratio is around 1.3 for pans fed with a brine concentrated from the water of the Dead Sea. Less than a fourth as much sodium chloride is harvested from pans operating on the carnallite equilibrium brine from the well as from pans fed with concentrated Dead Sea brine, and only one eighth of the evaporation is required.

Addition to the pan bitterns of fresh water equivalent to the evaporation, followed by recirculation underground, dissolves more carnallite and a small amount of halite. In this way the least amount of water is required and disposal of the bitterns is less of a problem. If fresh water is used in greater proportion due to recovery of magnesium chloride from the decomposition liquors, then carnallite is in turn decomposed underground and potassium chloride is left behind in a matrix of undissolved halite. Depending on the geometry and extent of the deposit it may be possible to recover such potassium chloride from the underground deposit by taking advantage of concentration gradients as the pool develops.

An evaluation of the particular deposit is required to determine if solution mining of the deposit offers an economic basis for competition with potash from other sources. Several favorable factors, including lower initial investment in pans, better feed grade, and less volume to pump compared to producers using natural brines, may more than compensate for the cost of deep well drilling and pumping.

A 250,000 ton per year plant to produce potash by solution mining and solar evaporation has the potential to also produce about 1.9 million tons of magnesium chloride as bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$).

Method of Processing Brines for Potash Recovery

For economic reasons, the recovery of magnesium chloride from natural brines or from brines synthetically produced by solution mining of carnallite cannot be divorced from potash operations. This discussion is therefore limited to a few typical brines which have present or potential value as sources of potash. In such operations magnesium chloride has, up to now, been rejected as an essentially valueless waste after the crystallization of carnallite.

The feed brines, which contain from 0.5 percent to perhaps as much as 2.0 percent of potassium chloride, are pumped from shallow wells or brought by systems of gathering ditches or canals to the first solar evaporation pans. The minimum economic size for a potash plant operating on dilute brines in which the first stable potash phase is carnallite is considered to be in the order of 250,000 tons per year of product. The feed rate for a plant of this size may vary from 20,000 to 35,000 gallons per minute depending on season and the initial concentration. Evaporation rates vary widely with the season, so pumps, pipelines, and canals are sized for maximum flow. Typical evaporation rate data for the Dead Sea are shown in Figure 1.

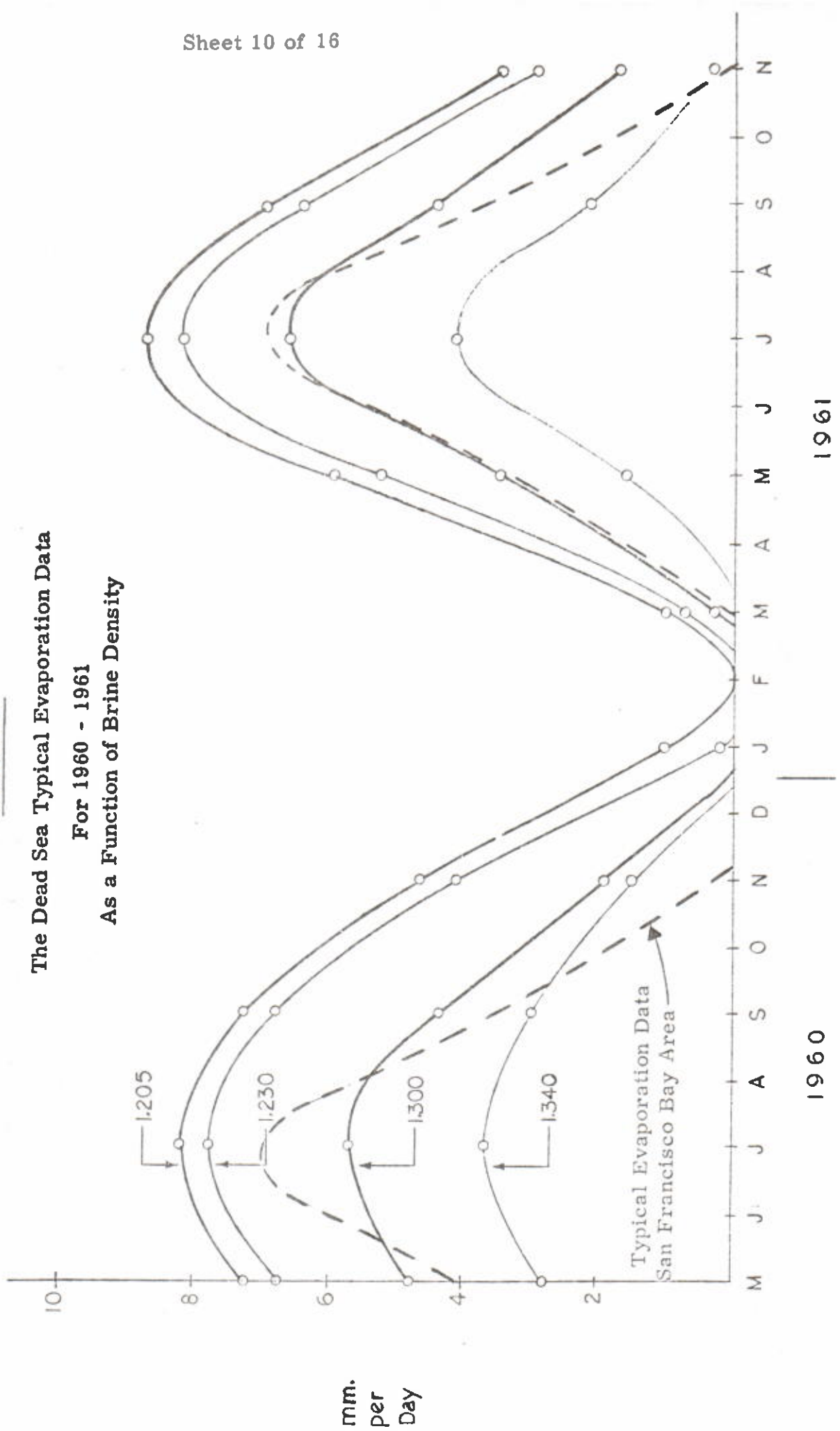
The solar pans are sized for the average net evaporation rate, which is determined empirically. The areas are quite large and may range from 20 to 40 square kilometers for a plant of the indicated size depending on initial brine concentration. The number and shape of the pans is generally fixed by the terrain. Preferably the pan borders are built on contour lines whose elevations differ by one meter or less, with maximum tolerance in elevation of the pan bottoms in the order of 30 cm. This specification largely determines the amount of cut and fill required. The pan bottoms, preferably, are composed of sedimentary claylike materials with low drainage rate. Cut and fill operations are held to a minimum, not only for economic reasons but also because of the danger of altering the soil substructure in such a way as to increase the rate of leakage.

As the brine flows by gravity through the pans, evaporation takes place and halite is deposited on the pan bottoms. For a plant capable of a production rate of 250,000 tons per year of potash, the salt tonnage produced is immense and may range upward from 2,000,000 tons per year. This salt is deposited on the pan bottoms in the first one half to two thirds of the solar pan area.

In a year's time more than 17,000,000 tons of water is evaporated. For illustration only, if natural gas were used to accomplish an equivalent evaporation, the cost for fuel alone would approach \$1,000 an hour.

FIGURE 1

The Dead Sea Typical Evaporation Data
For 1960 - 1961
As a Function of Brine Density



In locations remote from the seaboard, the salt has little economic value. Nevertheless, it must be removed from the pan bottoms periodically, or new pan areas must be put into production. Regardless of the way the operator chooses to solve the problem of halite build-up, costs are incurred which may range from \$0.20 to \$0.40 for a ton of product.

When the brine reaches a density of about 1.29, it is transferred to a second pond area where carnallite crystallizes. In some cases where the ratio of potassium to magnesium chloride is relatively high, potassium chloride may form as the first stable potash phase. On brines relatively high in sulfate some loss of values may occur from formation of polyhalite, and kainite as well as kieserite may crystallize in the final pans.

The brine is discharged from the carnallite ponds at a density of about 1.35. Compared to the initial feed brine the ratio of magnesium chloride to water has been improved from 0.16 to 0.45. A mixed crop of carnallite, together with a relatively small amount of halite, is recovered from the ponding area by dry methods or by dredging. Potash is recovered from the harvest by decomposition followed by flotation or selective leach-crystallization. The brine from decomposition of carnallite may be recycled to the carnallite ponds or used as a relatively pure source of magnesium chloride for production of bischofite. The schematic flowsheet for pan operations, decomposition, and bischofite production is shown in figures 2, 3 and 4.

THE PRODUCTION OF BISCHOFITE FROM CARNALLITE DECOMPOSITION LIQUOR

By evaporation and fractional crystallization bischofite may be prepared from a liquor in equilibrium with carnallite with a degree of purity limited only by economic considerations. Special problems may be encountered when the brines rejected from the final solar pans are in equilibrium with both carnallite and kieserite, but plants in operation and proposed at the Dead Sea do not encounter this problem. Due to the rather high concentration of CaCl_2 in the Dead Sea brine, the small amount of sulfate is rejected with the salt in the initial pans as anhydrite, or discharged in the pan bitterns. At Wendover, Utah, the sulfate concentration is initially high enough to form kainite, kieserite, and carnallite in the final pans, but the potash values are recovered by leaching in place.

The liquor from the decomposition of carnallite may be sent to a separate ponding area. In the first stage evaporation carnallite and halite are deposited. The solid phases join the main plant feed stream and are decomposed. The solid phases join the main plant feed stream and are decomposed. The liquor in equilibrium with bischofite is evaporated essentially to dryness, perhaps by

FIGURE 2

SCHEMATIC FLOWSHEET

Carnallite Recovery from Brines and Evaporites

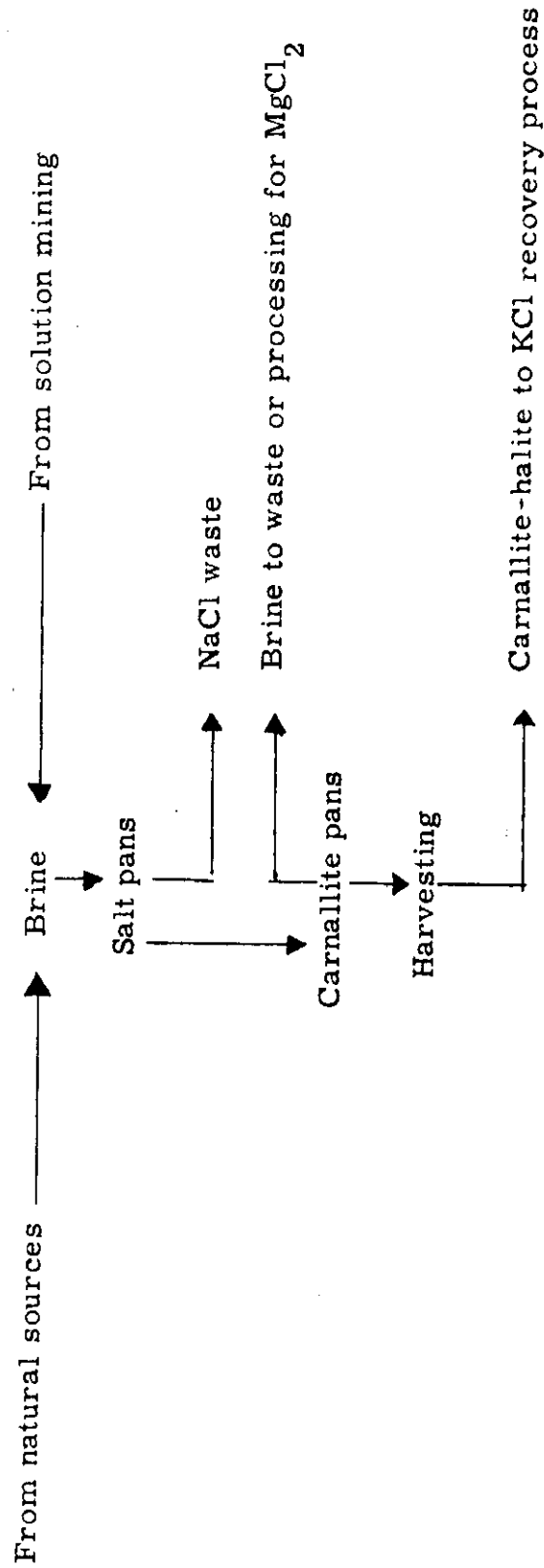


FIGURE 3

SCHEMATIC FLOWSHEET

Carnallite Conversion

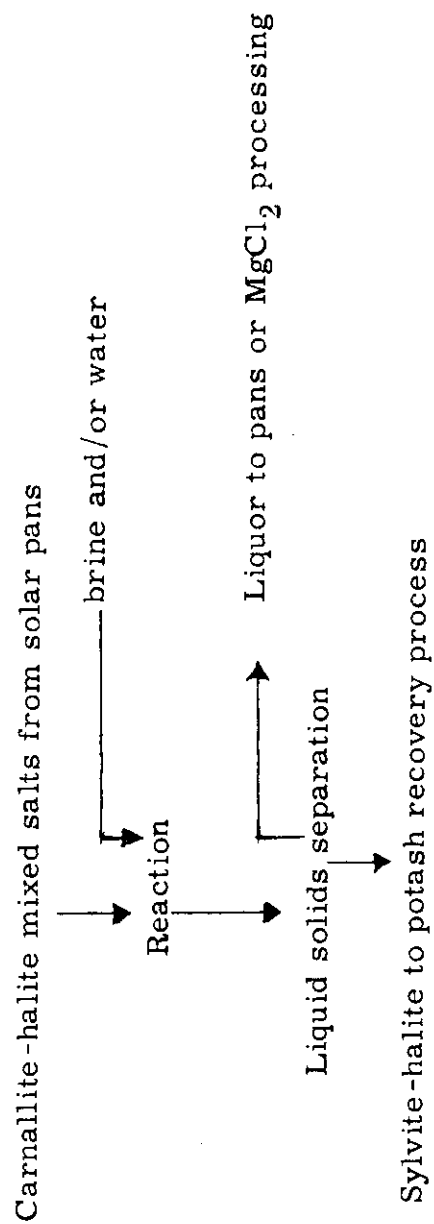
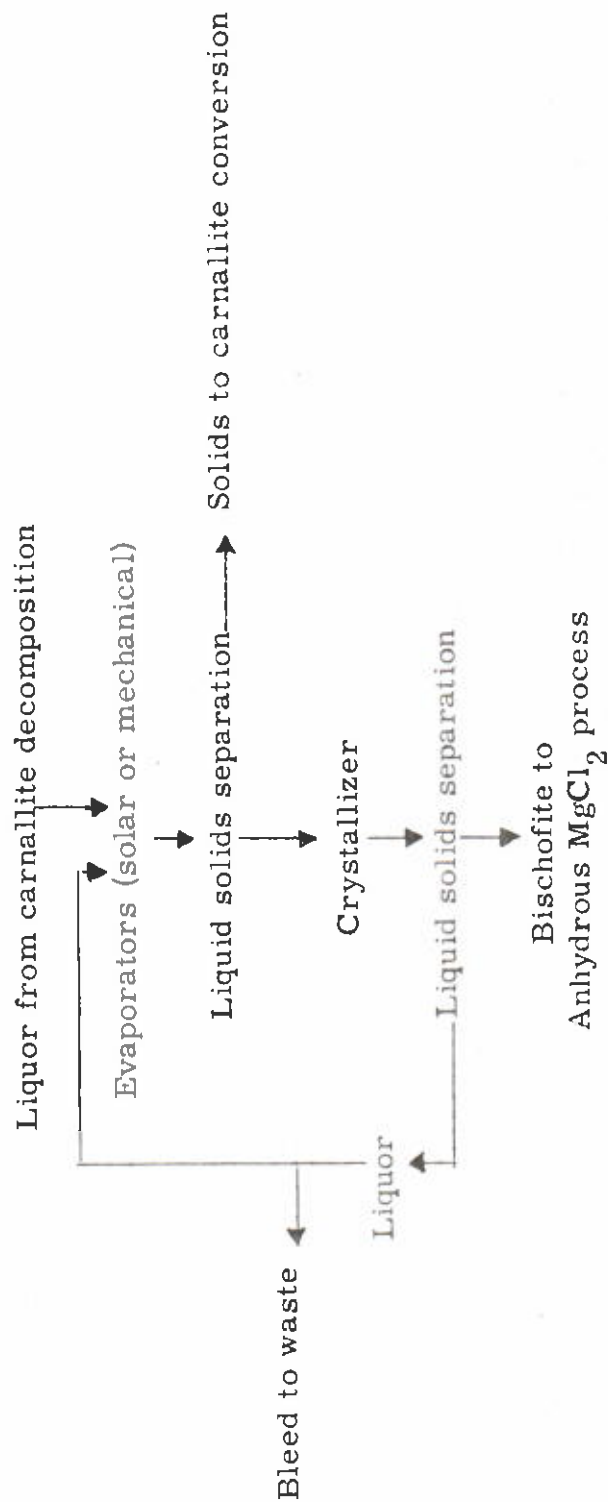


FIGURE 4

SCHEMATIC FLOWSHEET

Production of Bischofite ($\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$)



a combination of solar and mechanical means. Bischofite of almost any desired degree of purity can be obtained by recrystallization. Based solely on the carnallite stoichiometry and without regard to losses, over 300,000 tons per year of magnesium chloride hexahydrate or bischofite may be produced by a potash plant of the indicated size solely from the decomposition liquors. In addition to this the pan bitterns are a potential magnesium chloride source that is an order of magnitude larger.

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